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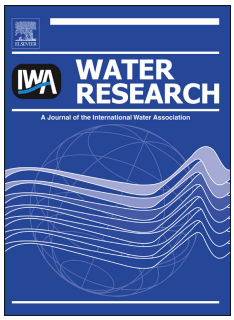

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Authors: Matthew Lee, Ralf Cord-Ruwisch, Mike Manefield

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A process for the purification of organochlorine contaminated activated carbon: sequential solvent purging and reductive dechlorination.

Matthew Lee[a,*], Ralf Cord-Ruwisch[b] and Mike Manefield[a]

a Centre for Marine BioInnovation, University of New South Wales, Sydney Australia 2052

b School of Biological Science and Biotechnology, Murdoch University, South Street Murdoch, Western Australia, 6052

* Author for correspondence, mattlee@unsw.edu.au

Abstract

A system for the purification of organochlorine contaminated activated carbon is described. The system involves a continuous flow of aqueous ethanol to purge organochlorines from activated carbon. The organochlorine laden solvent is simultaneously treated with zero valent zinc as the bulk electron source, water as the proton source and the electron shuttle cyanocobalamin as a catalyst for reductive dechlorination. The system was characterised by performing batch reactions and extractions before being applied in a continuous flow system. In particular the ratio of water to ethanol in the system needed to be optimised. Water is needed for the reductive dechlorination reaction whilst it is not conducive to the extraction process. An 80% ethanolic solution was found to give optimal reductive dechlorination rates without compromising extraction of organochlorines from activated carbon. Of three electron shuttles evaluated cyanocobalamin was discovered to be the most relevant to the system with respect to reductive dechlorination rates and its ability to avoid absorption to activated carbon.

Key words: activated carbon, zero valent zinc, organochlorines, reductive dechlorination, electron shuttle, cyanocobalamin.

1. Introduction

Organochlorines represent a large group of synthetic compounds used in a broad range of applications. They are used in dry cleaning solvents, flame retardants, paint strippers, industrial degreasers, pesticides, herbicides and fungicides. Many organochlorines are suspected carcinogens and therefore their discharge into the environment combined with their resistance to natural degradation poses a real threat to the environment and therefore human health.

Activated carbon adsorption is the most common means of purification of water and gas streams contaminated with organochlorines (Karimi et al., 1998; Cooney et al., 1983). However, there is no chemical change to the absorbed organochlorines and therefore the process merely relocates the target pollutant. If the activated carbon is to be re-used it must be treated to remove the pollutant. Alternatively, the carbon must be safely stored at the owners' expense or loss of space. The economics of activated carbon lean toward regeneration and reuse over reusing virgin activated carbon or stockpiling the polluted activated carbon (Cooney et al., 1983).

A number of activated carbon regeneration techniques have been proposed in the literature. These include wet peroxide oxidation (Okawa et al., 2007), solvent extraction (Cooney et al., 1983; Martin and Ng, 1987), and bioremediation (Nakano et al, 2000). Thermal treatment however, is the most commonly used method for activated carbon regeneration (Álvarez et al., 2004; Ania et al., 2004). The energy requirements for maintaining the high temperature required

for the process make it costly and therefore the cost effectiveness of this technology is minimal in addition to a loss of 5-15% of carbon due to its burn off (Álvarez et al., 2004). Also the thermal treatment of organochlorines is considered particularly difficult because of their relative stability and the possibility of producing undesired gaseous products such as hydrochloric acid (Urano et al., 1998).

Solvent extraction has been proposed as a viable alternative to thermal regeneration of activated carbon (Cooney et al., 1983; Martin and Ng, 1987). The advantages of solvent extraction over thermal desorption are: 1) no carbon attrition, 2) no degradation of the carbon pore structure and 3) little loss of absorptive capacity if the desorptive solvent is thoroughly removed. However, in a situation where solvent extraction is used to purify organochlorine polluted activated carbon the chemistry of the desorbed compounds is not altered and so the questions still remains as to what to do with the residual organochlorine contaminated solvent. Treatment of desorbed organochlorines by reductive dechlorination is a plausible solution.

The carbon-chlorine bond has a high oxidation state and as such the estimated reduction potential range for alkyl halides is between 0.5 - 1.5 V (Vogel et al, 1987). Reductive dechlorination is a chemical process in which organochlorines are transformed into hydrocarbons when they react with a suitable electron donor (reductant) in the presence of a proton source. Zero valent metals such as zinc and iron, with reduction potentials of -760 and -440 mV respectively have been shown to be excellent electron donors in the reductive dechlorination of toxic chlorinated methanes and ethanes to innocuous hydrocarbon end products (Song and Carraway, 2005; Gillham and O'Hannesin, 1994; Arnold et al., 1999;

Johnson et al., 1996). The reduction potentials of both zinc and iron are such that the hydrolysis of water is slow. This characteristic has lead to the installation of permeable zero valent metal barriers to remediate organochlorine contaminated groundwater (Gillham and O'Hannesin, 1994; Arnold et al., 1999; Johnson et al., 1996; Matheson and Tratnyek, 1994). In such installations the groundwater serves as the proton donor to effect the reductive dechlorination of the organochlorine while the slow hydrolysis of water by the zero valent metals ensures reductive dechlorination activity over many years.

Cyanocobalamin has been shown to increase the rate of reductive dechlorination of perchloroethene (PCE) and trichloroethene (TCE) by zero valent zinc and iron in aqueous reaction systems (Kim and Carraway, 2002). Redox active compounds such as cyanocobalamin can accept electrons from an electron donor and then transfer them to an electron acceptor ultimately remaining chemically unchanged. There are a number of naturally occurring classes of compounds that can act as electron shuttles including: quinones, phenazines, viologens and organo-metallic complexes (Kim and Carraway, 2002; Fultz and Durst, 1982). Of the organo-metallics cyanocobalamin has been extensively studied with respect to catalysis of reductive dechlorination reactions with various soluble and insoluble electron donors. It has been demonstrated that the reactions involving iron or zinc reduction of PCE or TCE had significantly lower activation energy when cyanocobalamin was included as a catalyst (Kim and Carraway, 2002).

In this study we have developed a regeneration technology for activated carbon contaminated with organochlorines. The process involves the integration of solvent purging of organochlorine polluted activated carbon followed by their reductive dechlorination using zero valent zinc as the

bulk electron donor. The process also employs cyanocobalamin as an electron shuttle to enhance reductive dechlorination rates and water as the bulk proton source. The desorption properties of organochlorines from activated carbon with various water soluble solvents were considered and the reductive dechlorination of organochlorines was optimised in terms of solvent water composition, cyanocobalamin concentration, reaction temperature and zinc particle size. Finally, the impact of the regeneration process on the absorptive properties of activated carbon was characterised.

2. Materials and Methods

2.1 Chemicals.

hexachloro-1,3-butadiene (HCBD), perchloroethene (PCE), carbon tetrachloride (CTC), zinc dust (<10 μm, 0.18 m^2/g), zinc particles (20 mesh, <0.01 m^2g^{-1}), ethanol, methanol, N,N-dimethyl formamide, 2-propanol, acetone, acetonitrile, cyanocobalamin, neutral red and anthraquinone-2,6-disulphonic acid, granular activated carbon (untreated, 4-8 mesh, 1070 m^2g^{-1}), were all used as received from Sigma-Aldrich chemicals (Australia). Stock solutions of organochlorines for reductive dechlorination optimisation reactions were prepared in degassed ethanol in an anaerobic chamber. The solutions were stored in glass flasks sealed with Teflon® faced septa.

The surface area of the activated carbon and metal surfaces used in this work were determined using a Micromeritics Tristar surface area and porosity analyzer using the Brunauer, Emmet, and Teller (BET) model. Samples were pretreated by vacuum drying at 150°C for 3 hours.

2.2 Batch organochlorine absorption and desorption from activated carbon.

Activated carbon (20 g), which had been washed with water and dried at 100°C for 12 hours, was added to a saturated aqueous solution of CTC, PCE and HCBD. The mixture was stirred vigorously with a magnetic stirrer for 24 h allowing the organochlorine time to equilibrate with activated carbon. The activated carbon was then filtered to remove excess water. The amount of absorbed organochlorines to activated carbon was determined to be 55.7 mgg^{-1} (CTC), 29.3 mgg^{-1} (PCE) and 2.9 mgg^{-1} (HCBD). This determination was achieved by extracting sub-samples (3 x 1g) of the activated carbon with ethyl acetate (5 x 20 ml) each extraction lasted for 1 hour. The extracts were then analysed by gas chromatography. Sub-samples of organochlorine polluted activated carbon (3 x 1 g) were then extracted with 50 ml of the test solvent with agitation (150 rpm, horizontal shaker) for 30 min in 120 ml crimp sealed (Teflon® faced septa) flasks.

2.3 Batch organochlorine reductive dechlorination reactions.

Reductive dechlorination optimisation experiments were performed in 60 ml glass flasks filled with the required proportions of ethanol, water, electron shuttle (100 μM) and zinc dust (<10 μm, 0.18 m^2g^{-1}, 1 g per flask) or zinc particles (20 mesh, <0.01 m^2g^{-1}). The flasks were crimp sealed (Teflon® faced septa) and deoxygenated by sparging with argon for 20 min. The reactions were initiated by the introduction of the required volume of an ethanolic HCBD solution through the septum using a glass syringe. Reaction mixtures were vigorously stirred

using Teflon® coated magnetic stirrer bars. Reaction temperature was maintained at 55 ± 2 °C by submerging the reaction vessel in a water bath.

2.4 Cyanocobalamin, neutral red and AQDS absorption to activated carbon.

Glass flasks (60 ml) were filled with activated carbon (1 g) and 25 ml of an ethanol/water mixture containing cyanocobalamin, neutral red or AQDS (100 μM). The flasks were shaken for 24 h (150 rpm, horizontal shaker) to allow for the equilibration of the electron shuttle between solid and liquid phases. The residual electron shuttle in the liquid phase was then measured by UV/VIS spectroscopy at 362 nm for cyanocobalamin or 462 nm for neutral red. In the case of AQDS the compound was required to be in the reduced state for measurement at 450 nm. To achieve this 10 ml of the liquid phase was placed in Hungate tubes with zinc powder (100 mg, 1.54 mmoles). The tube was then crimp sealed with rubber septa, sparged with argon for 30 minutes and then agitated on a horizontal shaker (150 rpm) for 8 h at room temperature. The absorbance was measured by directly inserting the Hungate tubes into a UV/VIS spectrophotometer.

2.5 Activated carbon regeneration efficiency.

Glass flasks (3 x 500 ml) were charged with an aqueous solution of PCE (46 mgL^{-1}, 277 μM) and activated carbon (100 mg), the flasks were then crimp sealed (Teflon® faced septa) and agitated (50 rpm, horizontal shaker) for 24 h to allow the PCE to equilibrate between the activated carbon and the aqueous phase. The liquid phase was then analysed by gas chromatography in term PCE concentration to determine the amount absorbed by the activated carbon. The activated carbon was then purged with 80% ethanol (5 x 100 ml) to remove all

traces of PCE followed by water (5 x 100 ml) to remove all traces of ethanol. The procedure was repeated 5 times. The regeneration efficiency of the activated carbon is defined as:

$$\frac{\text{absorptive capacity after regeneration}}{\text{absorptive capacity virgin activated carbon}} \times 100$$

2.6 Description and operation of bench scale activated carbon regeneration unit.

The activated carbon regeneration unit (Fig. 1.) is comprised of an activated carbon containment vessel and a reduction vessel. The activated carbon containment vessel was made from polycarbonate tubing [300 mm x 50 mm (o.d.), 40 mm (i.d.)] holding approximately 100 g of activated carbon. The tube was capped by aluminum screw caps with Swagelok® fittings at each end. The reduction vessel was a modified 2.5 L Schott® bottle fitted with a 3 way union. The union allowed solvent flow in and out and headspace over pressure release. The two vessels were connected with stainless steel tubing and solvent flow was facilitated by a peristaltic pump at 100 ml per minute.

Under typical operating conditions contaminated activated carbon (100 g) was loaded into the activated carbon containment vessel and zinc granules (100 g, 1.54 mol.) were added to the reduction vessel. The system was purged with nitrogen for 15 minutes by opening valves 1 and 3 and closing valves 2 and 4 (Fig.1). The system was then charged with 2.5 L of 80% ethanol containing 20 μM cyanocobalamin. The metering pump was engaged to allow circulation of the solvent. The temperature was maintained at 50 ^{o}C by heating the reaction vessel on a hot plate. Liquid samples were extracted from the system by closing valve 2 and opening valve 3. As the system was sealed there could be no solvent loss and the production of hydrocarbon gases could be monitored via a pressure indicator. Periodically the over pressure was released into a Tedlar®

gas sampling bag by opening valve 4 (Fig. 1.). The gaseous hydrocarbons were analysed by gas chromatography.

2.7 Gas chromatographic analysis.

Headspace samples (100 µl) were withdrawn with a gas tight syringe and analysed manually using an Agilent Technologies 7890 gas chromatograph (GC) fitted with a flame ionisation detector and split/splitless inlet. Compounds were separated on a GasPro column (60 m x 0.32 mm (i.d.)). The following conditions were observed: helium mobile phase (3 ml/min); injection port temperature 250 °C, split ratio of 1:10; detector temperature 250 °C. The oven temperature remained at 100 °C for 8 minutes.

Liquid samples (1 ml) were withdrawn from the reaction mixture with a glass syringe and transferred to a glass crimp top vial. Samples were then analysed with an Agilent Technologies 7890 GC fitted with an electron capture detector and split/splitless inlet. Compounds were separated on a DB5 column (30 m x 0.32 mm (i.d.) x 0.25 µM (film thickness)). The following conditions were observed: helium mobile phase (1 ml/min); injection port temperature 250 ^{o}C, split ratio 1:200; detector temperature 250 °C, injection volume 1 µl. The oven temperature program was as follows: 40 °C for 1 min, 20 °C/min and then 300 °C for 1 min.

Aqueous ethanolic solutions were analysed with an Agilent Technologies 7890 GC fitted flame ionisation detector and split/splitless inlet. The following conditions were observed: helium mobile phase (1 $mlmin^{-1}$); injection port temperature 250^{o}C, split ratio 1:200; detector temperature 250 °C, injection volume 1 µl. the oven was maintained at 80 ^{o}C for 5 minutes.

3. Results

3.1 Recovery of organochlorines from activated carbon with various water miscible solvents.

To develop a suitable solvent for the extraction of organochlorines from activated carbon seven water soluble solvents were tested Table 1. The rank order in terms of desorbing ability was dimethyl formamide > acetonitrile > ethanol > acetone > 2-propanol > methanol. Note that this experiment was designed to compare solvents and was not optimised to achieve maximal extraction. Table 1 also lists the relative cost and toxicity of each solvent. Taking into account these three factors, ethanol was chosen as the most convenient solvent for the activated carbon regeneration process.

3.2 Recovery of organochlorines from activated carbon with ethanol water mixtures.

The impact of the addition of water to ethanol on organochlorine desorption was assessed in batch extraction experiments (Fig. 2). The extraction time in this experiment was optimised so that maximal extraction of organochlorines was achieved (12 h). Using a single tailed t-test (P = 0.05) there was statistically no significant difference in the extraction efficiency of CTC, PCE or HCBD from activated carbon with 80, 90 or 100% ethanolic solutions. This showed that the addition of water necessary for the subsequent reduction reaction did not compromise the extraction efficiency.

3.3 Reductive dechlorination reactions.

Batch reductive dechlorination reactions of HCBD in 90% ethanol involving zinc as the electron donor and cyanocobalamin, neutral red or AQDS as the electron shuttles or the reaction with no mediator produced chlorine free hydrocarbon gases. A number of different hydrocarbon end products were formed due to the possibility of either α-elimination or β-elimination of chlorine atoms (Fig. 3). The α-elimination pathway, which is the direct substitution of a chlorine with a hydrogen atom tended to predominate providing 1,3-butadiene (60%) as the major product. β-elimination where two adjacent chlorine atoms are removed resulting in unsaturation of the C-C bond generated but-1-ene-3yne and 1,3-butadiyne accounting for 10% and 20% respectively of C4 gases produced. The compound 2-butene was only observed in reactions involving cyanocobalamin, which can catalyse the reduction of one of the 1,3-butadiene double bonds.

The reaction kinetics for HCBD depletion in all four examples appeared to be first order after an initial lag phase (Fig. 4a-d). The lag phase is attributed to the initial mass transfer and absorption of HCBD to the zinc surface. The first order reaction constant (k (min^{-1})) for the depletion HCBD was derived from the slope of the line produced by plotting $ln(C_t/C_o)$ *vs.* time after the lag phase. The correlation coefficient (r^2) in all four treatments was > 0.95. The production of C4 gases appeared to be zero order in nature as there was a liner relationship (r^2 > 0.98) between C4 gas amounts and time. The comparative rate constants (min^{-1}) for HCBD depletion and rates of C4 gas production are summarised in table 2. There was a strong correlation in the rate of depletion of the HCBD ($r^2 = 0.99$) or the rate of C4 gas production (r^2 = 0.95) compared with the electron shuttle midpoint potential (E^o).

3.4 Adsorption of electron shuttles to activated carbon in ethanol/water mixtures.

The effect of ethanol/water composition with respect to adsorption of three electron shuttles to activated carbon was characterised. Neutral red and AQDS almost completely adsorbed to activated carbon with less than 1% of each shuttle remaining in solution regardless of the ethanol/water composition (Fig. 5). Cyanocobalamin however, was found not to absorb to activated carbon in ethanolic solutions above 40% (Fig. 5).

3.5 Reductive dechlorination reaction optimisation.

The reductive dechlorination of HCBD was optimised in terms of the concentrations of cyanocobalamin and water, the reaction temperature and the surface area of the zinc particles used. Rate constants for batch reductive dechlorination reactions of HCBD involving water in ethanol proportions between 0 and 50% are shown in Fig. 6. In the absence of water, little or no reaction was observed. Increasing the proportion of water stimulated the reaction rate where the first order rate constant maximised at -0.7 min^{-1} for reactions with 20 and 30% water. Further increases in water concentration lead to a decline in the reaction rate until reactions involving 50% water had less then half the maximal rate constant (-0.3 min^{-1}.)

The effect of cyanocobalamin concentration of the rate of HCBD reductive dechlorination was determined by batch reactions in 90% ethanol where the cyanocobalamin concentration varied between 0 and 20 μM. The rate of HCBD depletion increased substantially with the addition of cyanocobalamin. The rate constant increased five fold when reactions were amended with 1 μM cyanocobalamin and increased linearly (r^2 = 0.99) with cyanocobalamin concentrations up to 5

μM where a maximal rate constant of -0.37 min^{-1} was observed (Fig. 7). Cyanocobalamin concentrations above 5 μM did not impact further on the reaction rate.

Reaction temperature optimisation was achieved by performing batch reductive dechlorination reactions HCBD (1 mM) catalysed by cyanocobalamin (100 μM) at 22, 30, 45 and 60°C. The reaction rate increased exponentially with temperature (Fig. 8a.), and in accordance with the Arrhenius equation $k = Ae^{Ea/RT}$ (where k = rate constant, Ea = activation energy, R = ideal gas constant, T = temperature (degrees Kelvin)) a linear relationship was found when T^{-1} (Kelvin) was plotted against ln ((k (min^{-1})) ($r^2 = 0.96$) (Fig 8b).

In terms of use in the activated carbon recycling unit (Fig. 1.) the finer zinc powder (<10 μm) was washed out of the reaction vessel and became entrained in the activated carbon. Therefore coarser zinc granules (20 mesh, ~840 μm) which remained settled in the reactor were assessed. The surface areas of the two zinc types determined by BET surface area analysis were 0.18 m^2g^{-1} and <0.01 m^2g^{-1} respectively. In batch reductive dechlorination reactions in 90% ethanol involving cyanocobalamin as the electron shuttle reactions involving the zinc dust reactions had a first order rate constant of -0.49 min^{-1} whilst reactions involving granular zinc were seven times slower with a first order rate constant of -0.07 min^{-1} with respect to the disappearance of HCBD.

The optimised conditions described above were then applied to the integrated process involving activated carbon contaminated with CTC, PCE and HCBD (Fig. 9.). First order rate constants for the disappearance of the compounds were -0.58, -0.11 and -0.28 hr^{-1} for CTC, PCE and

HCBD respectively. Fully dechlorinated hydrocarbon gases were found to accumulate in the headspace of the reactor with the following rates: 70, 23 and 15 μMhr^{-1} for methane, C2 gases and C4 gases respectively. Additionally after the process was complete the ethanol was removed from the activated carbon column by purging with water. It was found that 99% of ethanol could be removed with 6 column volumes (300 ml) of water (Fig. 10.).

3.6 Effect of the regeneration process on the activated carbon adsorption characteristics. It was found that the activated carbon used in this study had a capacity of 160 mgg^{-1} for PCE. Multiple (x 5) regenerations of a single activated carbon sample demonstrated that the solvent extraction process had little effect on its capacity. On each regeneration occasion the PCE was completely removed from the activated carbon by purging with 80% ethanol. The ethanol was then removed by washing the activated carbon with water. The activated carbon was then allowed again equilibrate with an aqueous solution of PCE. On the first three occasions the adsorption capacity was greater than 96%, on the 4^{th} and 5^{th} regenerations the adsorption capacity was 89 and 88% respectively (Fig. 11)

4 Discussion

4.1 Organochlorine desorption with aqueous soluble solvent.

We have developed a process to regenerate spent activated carbon contaminated with organochlorines using ethanol, zinc, water and cyanocobalamin. The solvents tested for desorption were limited to those that are water miscible for two reasons. Firstly, the reductive dechlorination of organochlorines requires a proton source i.e. water (Kim and Carraway, 2002). Secondly, organic solvents will reduce the re-adsorptive capacity in future uses as they occupy

activated carbon pore space and therefore it must be possible to remove them by washing with water (Cooney et al., 1983). The ability to purge one, two and four carbon organochlorines, the cost and the toxicity of six solvents were compared. The order of effectiveness of organochlorine desorption is in agreement with previous studies where water soluble solvents were assessed for their ability to desorb phenol from activated carbon (Cooney et al., 1983; Pahl et al., 1973; Knickermeyer et al., 1973). N,N-dimethyl formamide and acetonitrile were the most effective solvents, however both are highly toxic and expensive. Ethanol and 2-propanol were the next most effective with similar cost. Ethanol was chosen because it is less toxic and less polar than 2-propanol.

4.2 Reductive dechlorination of hexachloro-1,3-butadiene (HCBD). HCBD is priority pollutant found in waterways soils and sediments world wide, it is toxic and possible human carcinogen (Laseter et al., 1976; Booker and Pavlostathis, 2000). Whilst there have been a number of studies on the reductive dechlorination of PCE and CTC with zero valent metals (Kim and Carraway 2002, Song and Carraway 2005) there is little known about the reductive dechlorination of HCBD (low et al., 2007). This study shows that HCBD can be reductively dechlorinated to gaseous chlorine free C4 gases with zinc as an electron donor and water as a proton donor. The rate of reaction was enhanced more than 100 fold by catalysis with three different water-soluble electron shuttles (an organo-metallic, a synthetic phenazine and a quinone sulphonate). In each case there was a lag in the production of chlorine free C4 gases compared with the consumption of HCBD, which can be explained by the sequential nature of the reductive dechlorination reaction. As observed by gas chromatography, intermediate partially chlorinated species were formed and consumed until chlorine free hydrocarbons

remained. The spectrum of partially chlorinated C4 congeners, ranging from penta chloro to mono chloro butadiene were identified by GC/MS and were consistent with previous studies (James et al., 2008; Booker and Pavlostathis, 2000). These partially chlorinated species were not quantified because pure compounds to serve as analytical standards were not available.

The inclusion of each electron shuttles accelerated significantly the reductive dechlorination reaction and it is interesting to note the linear correlation between reaction kinetics and the electron shuttle mid-point potential (table 2). This correlation demonstrates that reaction rates can be predicted based on the midpoint potential of the electron shuttle or that in a scenario where the midpoint potential of an electron shuttle is unknown it could be determined through reaction kinetics.

4.3 Effect of solvent water content.

The increase in the first order rate constant with increasing water concentration observed in this work is similar to that observed in a previous study involving the electrochemical reductive dechlorination of carbon tetrachloride in aqueous-dimethyl formamide (Arun-Prasad and Sangaranarayanan, 2000). In their study the authors propose that the presence of a polar component to the solvent system aids in the solvation of polar reaction products, which is a strong driving force for the reaction.

In our system it was observed that HCBD dechlorination rates decreased at water concentrations above 40%. HCBD has low water solubility (2 mgl^{-1} (James et al., 2008)). It is possible that the solubility and hence availability of this compound became limiting in reactions where the

water content exceeded 40%. Competition for the zinc surface could also explain the attenuated reaction rate at water concentrations above 40%. There are three reactions occurring at the zinc surface including the electrolysis of water, the reduction of cyanocobalamin and the unmediated reduction of the organochlorine. Therefore, at high water concentrations it could be that cyanocobalamin is out competed for the reactive zinc surface.

Having established that the optimal water concentration for the reductive dechlorination reaction is 20% it was necessary to assess how changing the polarity of the extraction solvent by adding water might affect the extractability of the organochlorines from activated carbon. It was found that there was little effect on the extractability of organochlorines until the water proportion exceeded 40%.

The impact of increasing the water proportion was also tested with respect to the absorbance of the three electron shuttles to activated carbon. In a process where solvent extraction and reductive dechlorination are combined in a continuous flow system there is the potential for the electron shuttle to adhere to the activated carbon. It was found that there was no absorption of cyanocobalamin to activated carbon until the water proportion exceeded 20%. However, the other potential electron shuttles tested (neutral red and AQDS) adhered to activated carbon even in 100% ethanol making them unsuitable for use in a process where the activated carbon solvent extraction and reductive dechlorination are combined in a continuous flow loop.

4.4 Cyanocobalamin concentration optimisation. A previous study demonstrated the cyanocobalamin concentration dependency of TCE reductive dechlorination in aqueous systems

(Kim and Carraway, 2002). They found the reaction rate increased linearly with increasing cyanocobalamin concentrations between 0 and 0.125 μM. A maximal cyanocobalamin concentration was not elucidated. Here we characterised the relationship between cyanocobalamin concentration and reaction rate in aqueous ethanolic solutions and determined the maximal cyanocobalamin concentration. Given the cost of cyanocobalamin it is desirable to maximize the reaction rate while minimising the amount of cyanocobalamin used. A linear correlation was found between cyanocobalamin concentration and the first order rate constant and cyanocobalamin concentrations beyond 5 μM had no additional impact on the reaction rate. At this concentration the zinc surface area is likely to become the limiting factor.

4.5 Temperature optimisation. Batch reductive dechlorination reactions were carried out at four different temperatures to determine if significant gains in reaction rate could be achieved by increasing the reaction temperature. A ten fold increase in reaction rate was observed between 22 °C and 60 °C. An aqueous/ethanolic solution of cyanocobalamin was reused 10 times in reactions exceeding 50 °C with no effect on the rate of reductive dechlorination of HCBD.

In accordance with the Arrhenius equation a linear relationship was found when plotting the inverse of temperature (K) against the natural log of the experimentally observed rate constants (min^{-1}). From this plot the activation energy for the cyanocobalamin catalysed zinc driven HCBD reductive dechlorination reaction was determined to be 51 $kJmole^{-1}$. The activation energy of mass transfer controlled reactions is 10-42 $kJmole^{-1}$ (Kim and Carraway, 2002). As the activation energy exceeds this range this suggests that the rate limiting step is the chemical reaction at the zinc surface not mass transfer to the zinc surface.

4.6 Zinc surface area consideration. Combining the various aspects studied in batch reactions into a continuous flow system for the treatment of organochlorine contaminated activated carbon was a matter of connecting two vessels with a peristaltic pump. One of the intended purposes of having two vessels was to prevent the activated carbon being entrained with zero valent zinc particles. It was found in initial trials that finely divided zinc dust (<10 μm, 0.18 m^2g^{-1}) became suspended in solution and moved from the reduction vessel into the desorption vessel. In contrast, the zinc granules with size of ~840 μm, <0.01 m^2g^{-1}) in diameter remained settled in the reaction vessel however, displayed a 7 fold reduction in reaction rate due to the large reduction in surface area. This correlation between zinc surface area and reaction rate is consistent with a previous study (Kim and Carraway, 2002). In there study a four fold increase in the zinc surface area gave rise to a three fold increase in the first order reaction rate constant for the cyanocobalamin mediated reductive dechlorination of trichloroethene.

With respect to zinc consumption, the zinc to HCBD ratio is 6:1 according to the reaction stoichiometry: $6Zn + 6H_2O + C_6Cl_6 \rightarrow 3Zn^{2+} + 6Cl^- + 3Zn(OH)_2 + C_4H_6$. In the batch reactions described there is a 50 fold excess of the metal is used. In theory this suggests that the 50 reactions could be performed before changing the zinc. However the diminution of the reactive surface due to its oxidation would probably curtail its utility before 50 reactions could be performed.

4.7 Effect of solvent extraction on activated carbon re-adsorption characteristics. The passive nature of solvent extraction is one of its main advantages. This technique allows for

removal of the activated carbon pollutant with out loss of carbon or damage to its porous structure (Cooney et al., 1983, Martin and Ng 1987). One important aspect of the solvent extraction process is that the desorbing solvent must be removed from activated carbon. If the solvent remains within the porous structure of the activated carbon it will reduce the absorptive capacity in subsequent uses (Cooney et al., 1983, Martin and Ng 1987). Hence this study was limited to water soluble solvents so that they could be removed from the activated carbon by simply washing with water. In terms of the activated carbon regeneration unit, 99% of ethanol could be removed from the activated carbon column with 300 ml (or six column volumes) of water Here we demonstrate that multiple adsorption of a desorption of PCE had little effect on the re-adsorptive capacity of a single activated carbon sample where after 5 recycles a 12% drop in capacity was observed. This compares well with a previous study where the capacity of activated carbon for phenol dropped and stabilised by 20% after 5 recycles (Cooney et al., 1983). There is no one clear reason why there should be any drop in adsorptive capacity assuming all the solvent is removed. Perhaps after multiple recycles small mounts of insoluble impurities in either the water or ethanol accumulate in the porous structure. A more detailed investigation of activated pore characteristics is required to shed light on this question.

4.8 Conclusion. A novel system for the purification of organochlorine contaminated activated carbon has been described. The system uses solvent extraction with 80% ethanol to purge the organochlorines from the activated carbon with simultaneous reductive dechlorination reactions to convert toxic organochlorines to innocuous hydrocarbon gases. The reductive dechlorination reaction was driven by zero valent zinc and protons were provided by water. Reaction rates were enhanced by catalysis with cyanocobalamin and increases in temperature. Unlike existing

technologies used for regenerating activated carbon this process is not energy intensive and has negligible effects on the absorptive properties of granular activated carbon.

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5. References

Álvarez, P.M., Beltra´ n, F.J., Gómez-Serrano, V., Jaramillo, J., Rodríguez, E.M., 2004. Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol. Water Res. 38, 2155–2165.

Ania, C.O., Menéndez, J.A., Parra, J.B., Pis, J.J., 2004. Microwave induced regeneration of activated carbons polluted with phenol. A comparison with conventional thermal regeneration. Carbon 42, 1383–1387.

Arnold, W.A., Ball, W.P., Roberts, A.L., 1999. Polychlorinated ethane reaction with zero-valent zinc: pathways and rate control. J. contam. Technol. 40, 183-200.

Arun-Prasad, M., Sangaranarayanan, M.V., 2000 Electrochemical reductive cleavage of carbon tetrachlorde in aqueous-nonaqueous binary solvents. J. Electroanal. Chem. 569, 127-134.

Booker, S.G., and Pavlostathis, R.S., 2000 Microbial Reductive Dechlorination of. Hexachloro-1,3-butadiene in a methanogenic enrichment culture. Water Res. 34, 4437-4445.

Cooney, D.O., Nagerl, A., Hines, A.L., 1983. Solvent regeneration of activated carbon. Water Res.17, 403–410.

Fultz, M-L, Durst R.A., 1982. Shuttle compounds for the electrochemical study of biological redox systems: a compilation. Analytica Chemica Acta. 140, 1-18.

Gillham R.W., O'Hannesin S.F., 1994. Enhanced degradation halogenated aliphatics by zero-valent iron. Ground Water. 32, 958-967.

James, D.L., Cord-Ruwisch, R., Schleheck, D., Lee, M.J., Manefield, M., 2008. Cyanocobalamin enables activated sludge bacteria to dechlorinate hexachloro-1,3-butadiene to non-chlorinated gases. Bioremediation Journal. 12, 177-184.

Johnson T.L., Scherer M.M., Tratnyek P.G., 1996. Kinetics of halogenated organic compound degradation by iron metal. Environ. Sci. Technol. 30, 2634-2640.

Karimi, A.A. Redman, J.A., Glaze, W.H., Stolarik, G.F., 1998. Evaluating an AOP for TCE and PCE. removal. J. AWWA. 89, 41–53.

Knickermeyer, W.W., Mayan, K. G., Bertrand, G. L., 1973. Organic desorption from carbon-III. The effect of solvent in the desorption of phenol from dry carbon. Water Res. 7, 1323-1330.

Kim, Y-H., Carraway, E.R., 2002. Reductive dechlorination of PCE and TCE by vitamin B_{12} and zero valent metals. Environ. Technol. 23, 1135-1145.

Laseter, J.L., Bartell, C.K., Laska, A.L., Holmquist, D.G., Condie, D.B., 1976. An ecological study of hexachlorobutadiene (HCBD). US NTIS (PB-252 671/3), Washington, DC, USA.

Low, A., Schleheck, D., Khou, M., Aagaard, V., Lee, M.., Manefield, M., 2007. Options for the in situ remediation of soil contaminated with a mixture of perchlorinated compounds. Bioremediation Journal, 11, 113 – 124.

Martin, R.J., Ng, W.J., 1987. The repeated exhaustion and chemical regeneration of activated carbon. Water Res. 21, 961–965.

Matheson L.J., Tratnyek P.G., 1994. Reductive dehalogenation of chlorinated methanes by iron metal. Environ. Sci. Technol. 28, 2045-2053.

Nakano, Y., Li, Q.H., Nishijima, W., Shoto, E., Okada, M., 2000. Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon. Water Res. 34, 4139–4142.

Okawa, K., Suzuki, K., Takeshita, T., Nakano K., 2007. Regeneration of granular activated carbon with adsorbed trichloroethylene using wet peroxide oxidation. Water Res. 41, 1045-1051.

Pahl, R.H., Mayhan, K.G., Bertrand, G.L., 1973. Organic desorption from carbon-II. The effect of solvent in the desorption of phenol from wet carbon. Water Res. 7, 1309-1322.

Song, H., Carraway E.R., 2005. Reduction of chlorinated ethenes by nano sized zero-valent iron: kinetic pathways, and effects of reaction conditions. Environ. Sci. Technol. 39, 6237-6245.

Urano, K., Kimura, C., Kobayashi, T., 1998. Actual condition of recycling and decomposing facilities for chlorinated solvent.Waste Manage. Res. 9, 56–65.

Vogel, T.M., Criddle, C.S., McCarty P.L., 1987. Transformations of aliphatic halogenated compounds. Environ. Sci. Technol. 21, 722-736.

Table 1. The mean percent recovery of organochlorines from activated carbon extracted with various water soluble solvents (± represent standard deviation (n=3)) along with their cost in Australian dollars (A$) per liter and toxicity (LD50 for rats).

Table 2. Comparison of rate constants for HCBD depletion and rate of C4 gas production in reductive dechlorination reactions in 90% ethanol with zero valent zinc as the bulk electron donor with electron shuttles (100 μM) and their mid-point potentials (E^o). ((a) Fultz and Durst, 1982; (b)Kim and Carraway, 2002).

Fig. 1 - Schematic diagram of the laboratory bench scale activated carbon regeneration unit.

Fig. 2 - The extraction of CTC (♦), PCE (■) and HCBD (▲) from activated carbon with various ethanol/water mixtures. Error bars represent standard deviation from the mean (n=3).

Fig. 3 - The structure and relative proportion of C4 gases produced via the zinc driven reductive dechlorination of HCBD in the presence of the electron shuttles cyanocobalamin, AQDS and neutral red. Note that 2-butene was only produced where cyanocobalamin was the electron shuttle.

Fig. 4 - The reductive dechlorination of HCBD (♦) to C4 gases (■) by zero valent zinc in 90% ethanol. Separate batch reactions were conducted in the absence of an electron shuttle (**A**) or in the presence of a 100μM of three different electron shuttles: anthraquinone-2,6-disulphonic acid (**B**), neutral red (**C**) and Cyanocobalamin (**D**). The dotted lines represent the line of best fit over

the time range used for the determination of first order rate constant (k (min^{-1})) for the disappearance of HCBD (♦) or the rate of C4 gas (■) production (μmol./min).

Fig. 5 - The absorption of the electron shuttles cyanocobalamin (♦), neutral red (■) and AQDS (×) to activated carbon in batch experiments with varying ethanol concentrations.

Fig. 6. - The effect of water concentration on the first order rate constant (k) for the reductive dechlorination of HCBD by zero valent zinc. The result demonstrates the optimal reaction rates occur with 20% water in ethanol

Fig. 7. - The effect of cyanocobalamin concentration on the first order rate constant (k) in the reductive dechlorination of HCBD by zero valent zinc in 90% ethanol. The result demonstrates that the optimal cyanocobalamin concentration is 5μM.

Fig. 8. - (**A**) the dependency of the first order reaction rate (k) on temperature (T) for the cyanocobalamin catalysed reductive dechlorination of HCBD by zero valent zinc in 80% ethanol. (**B**) The Arrhenius plot enabling the activation energy (E_a) for the reaction to be determined. E_a = -slope x R (ideal gas constant) = 6.16 x 8.31 = 51.2 kJ/mol.

Fig. 9. - The depletion of the organo chlorines CTC (♦), PCE (■) and HCBD (▲) (**A**) and the concomitant production of hydrocarbon gases methane (♦), C2 gases (■), C4 gases (▲) (**B**) in the treatment of organochlorine contaminated activated carbon, the trend line represents the time

period over which gas production rate was calculated. Organochlorines (**A**) and hydrocarbon concentrations (**B**) are defined in terms of their respective liquid and headspace volumes.

Fig. 10. - The removal of ethanol from the activated carbon column (100g) in the activated carbon regeneration unit by rinsing with water (1 column volume = ~50 ml).

Fig 11. - Activated carbon adsorption capacity for PCE throughout 5 cycles of PCE adsorption, desorption with 80% ethanol and water rinsing.

Solvent	CTC	PCE	HCBD	A$/L	LD50 (mg/kg rats)
ethanol	65.5±0.6	66.3±1.5	55.4±3.3	50	3450
methanol	55.1±8.8	52.0±11.5	59.8±8.1	50	7300
acetone	62.7±7.7	58.2±0.0	52.2±4.6	51	3000
acetonitrile	71.6±8.4	75.5±12.8	64.1±13.1	102	269
dimethylformamide	94.5±5.3	77.6±8.0	59.8±1.5	100	2900
2-propanol	80.5±3.9	55.1±5.0	48.0±1.5	48	3600

Shuttle name	E^o (mV)	Rate constant HCBD depletion (min^{-1})	Rate of C4 gas production ($\mu molmin^{-1}$)
No mediator		-0.004	0.03
AQDS	-185[a]	-0.007	0.09
Neutral red	-325[a]	-013	0.51
Cyanocobalamin	-600[b]	-0.41	0.88

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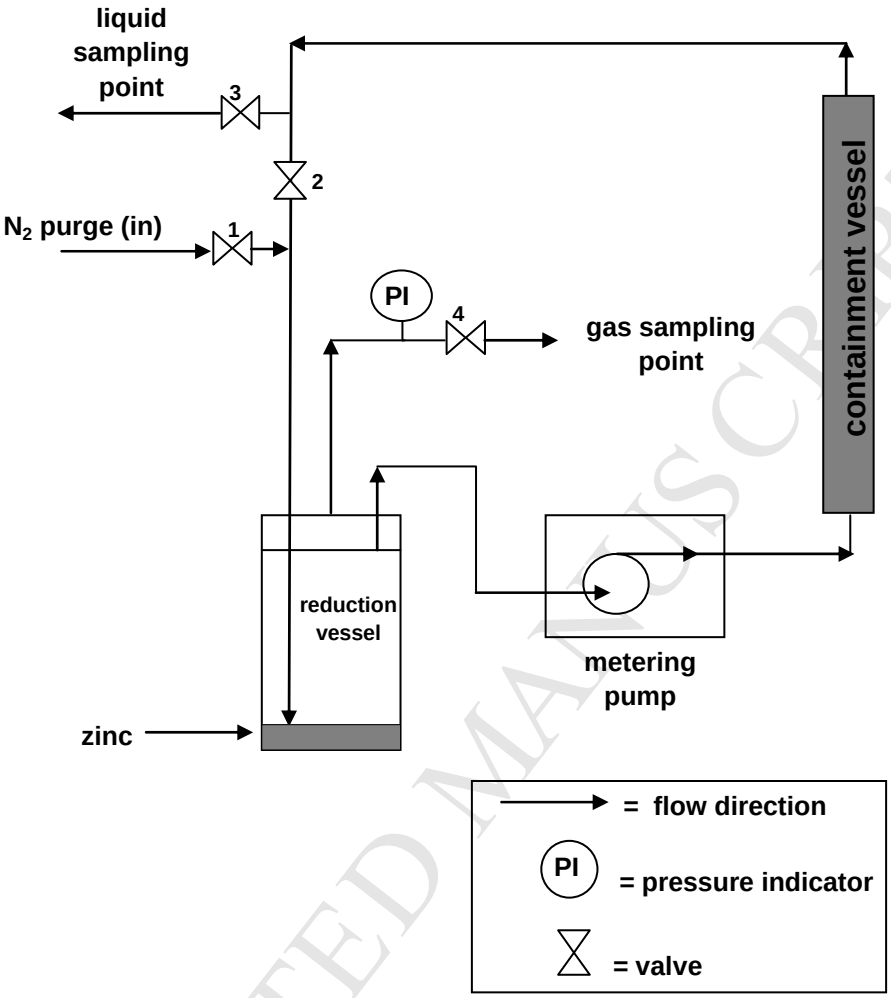

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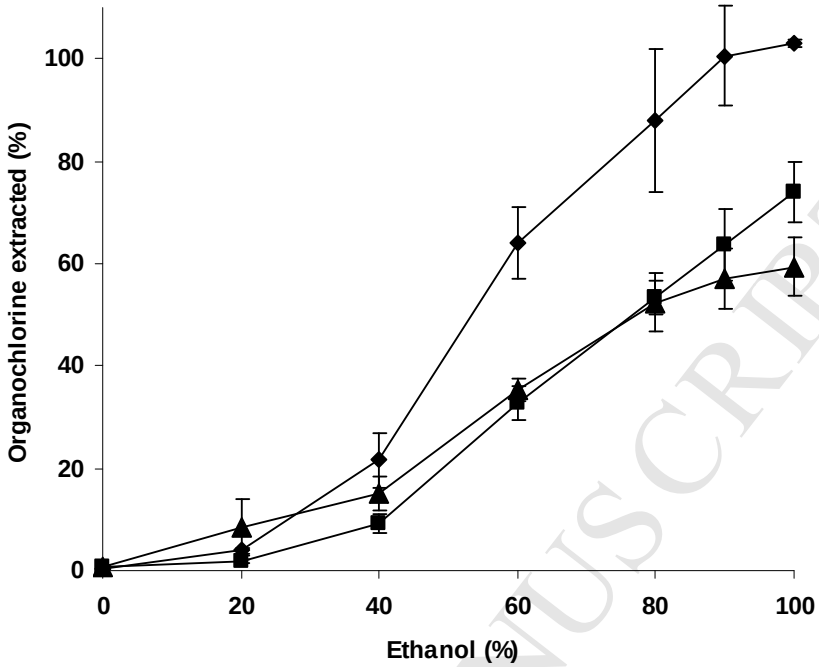

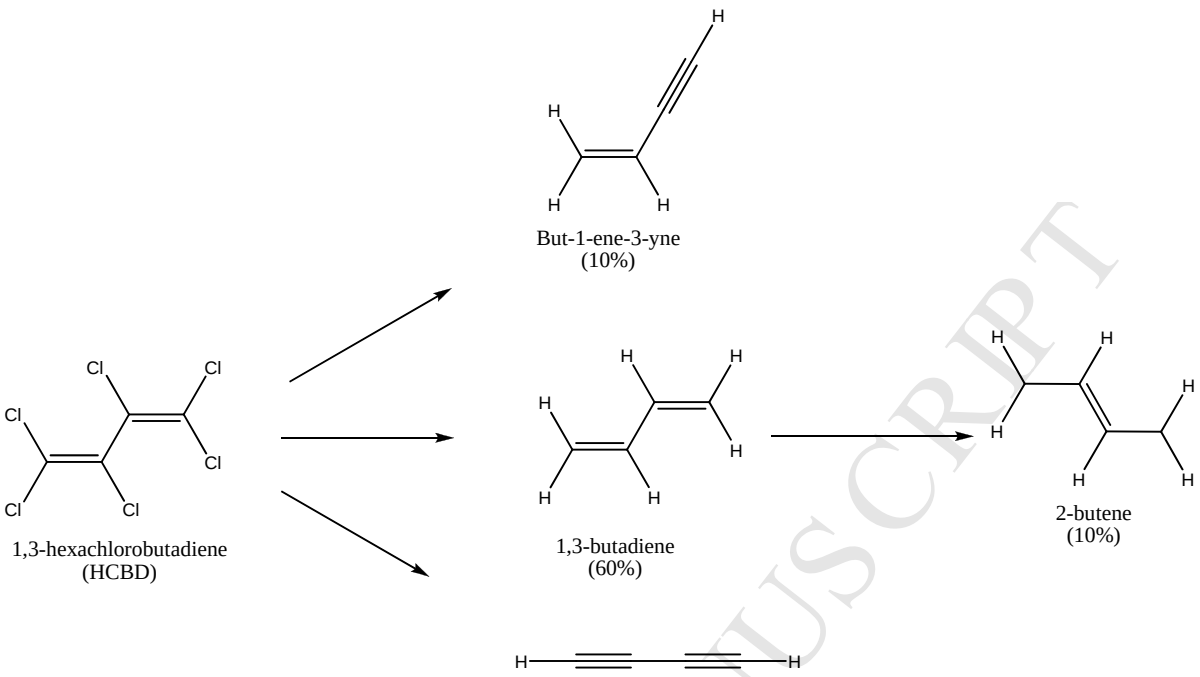

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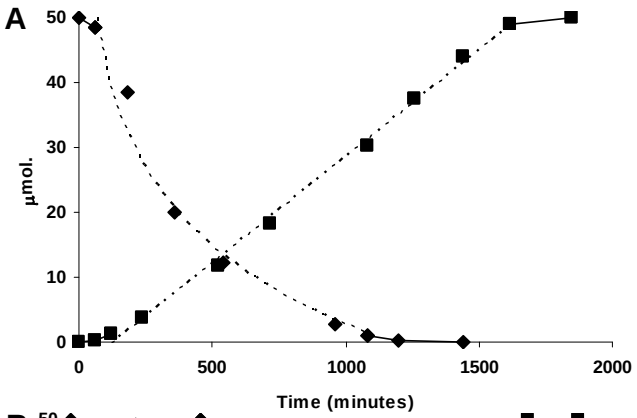

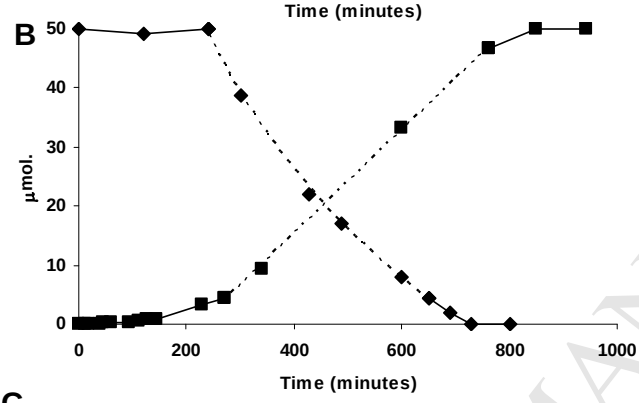

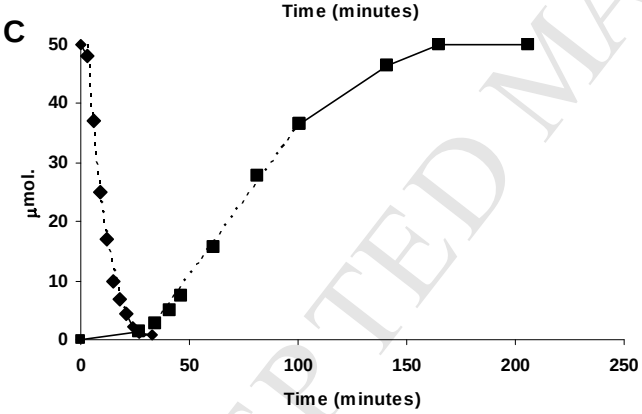

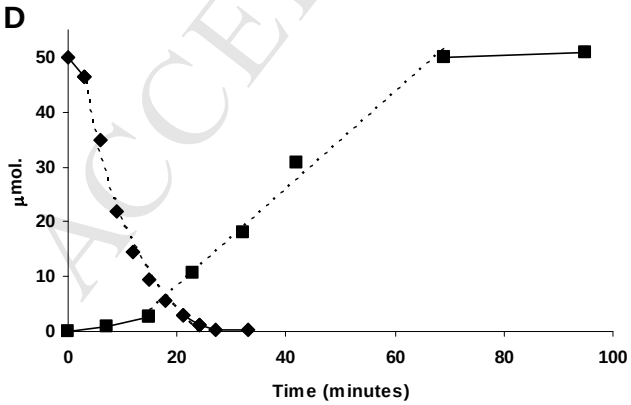

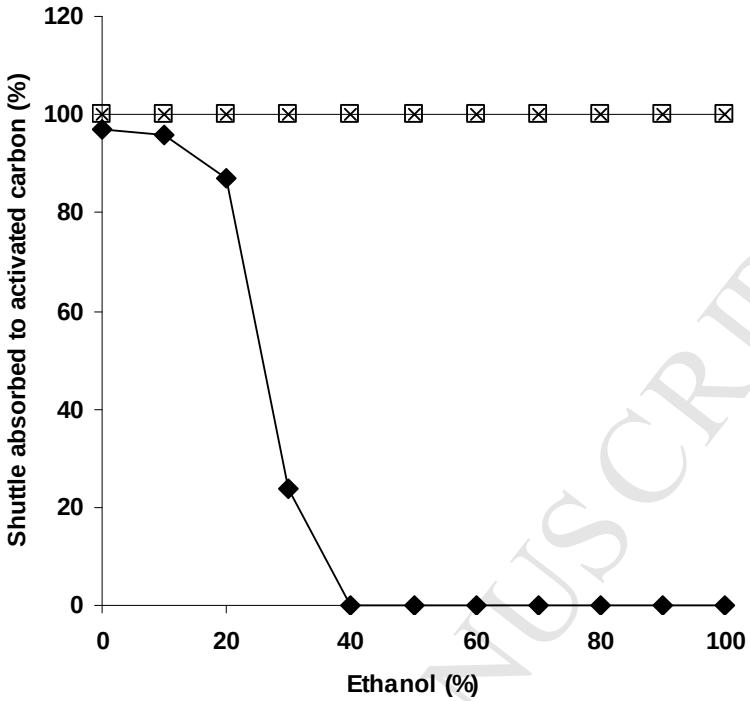

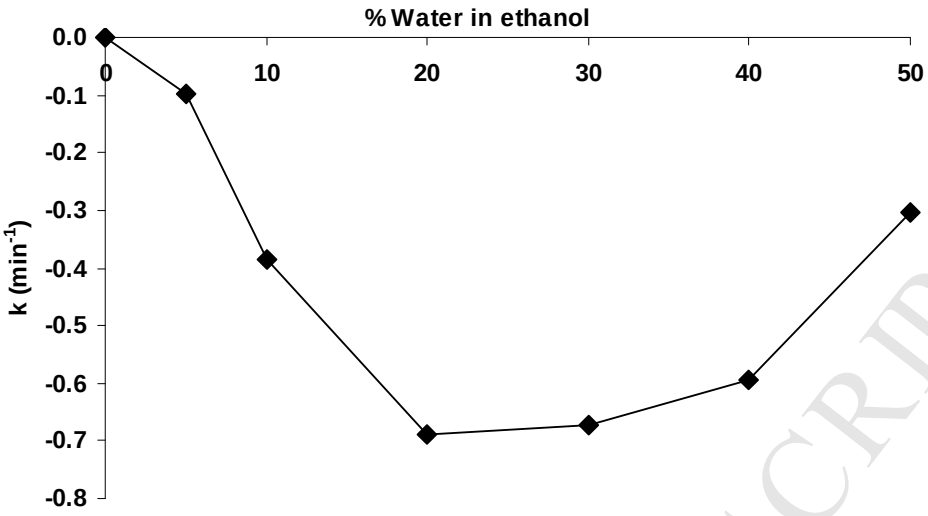

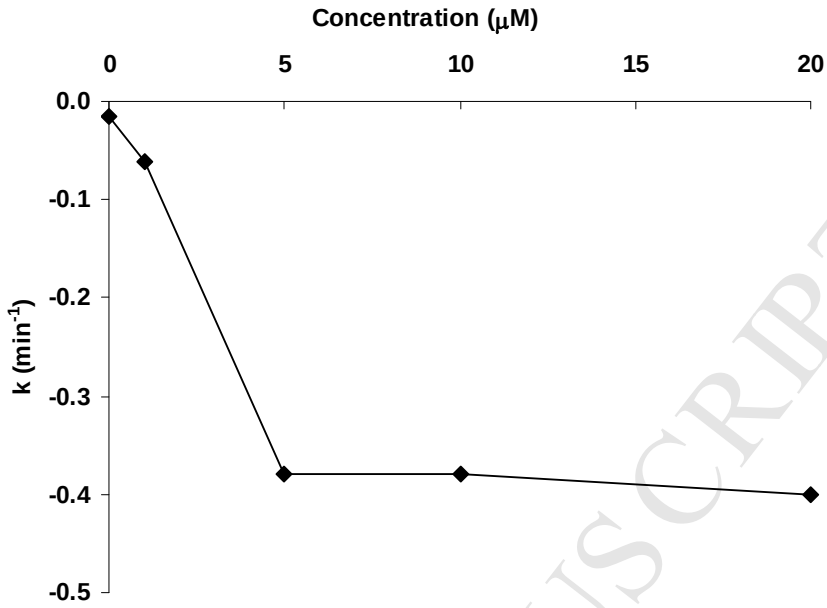

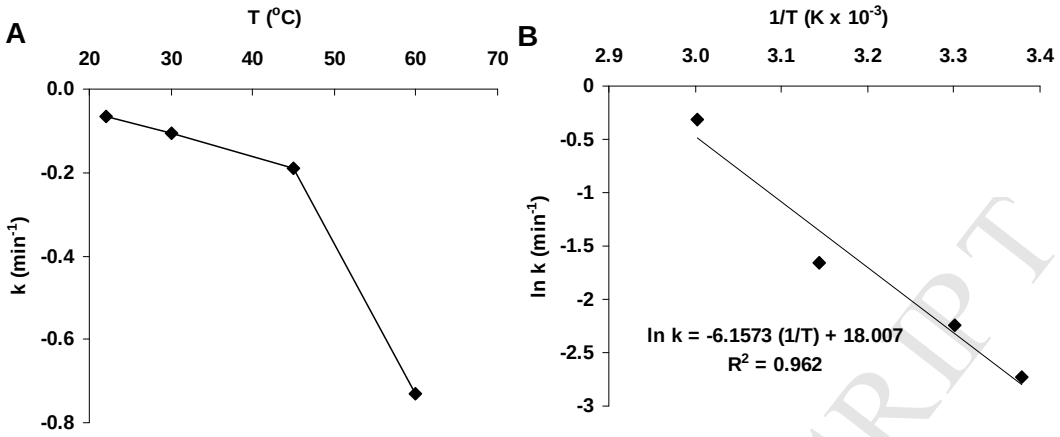

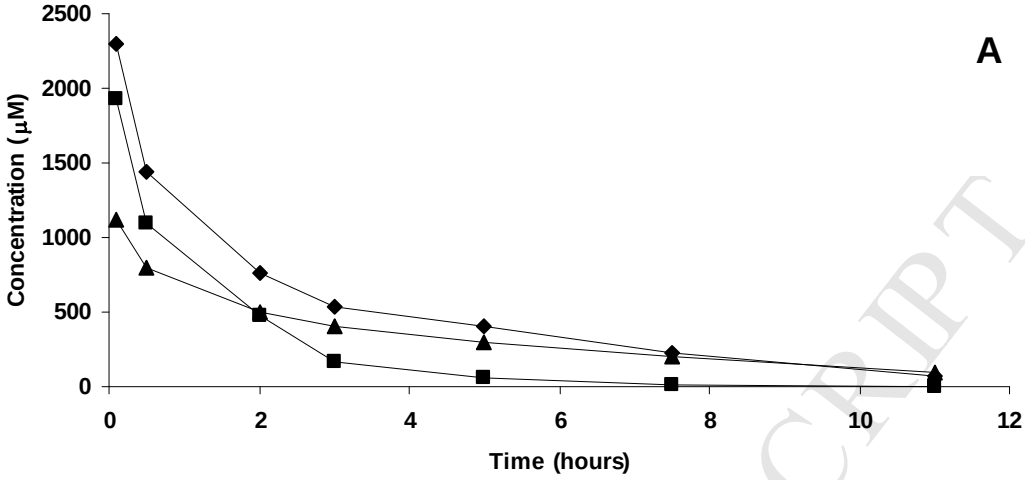

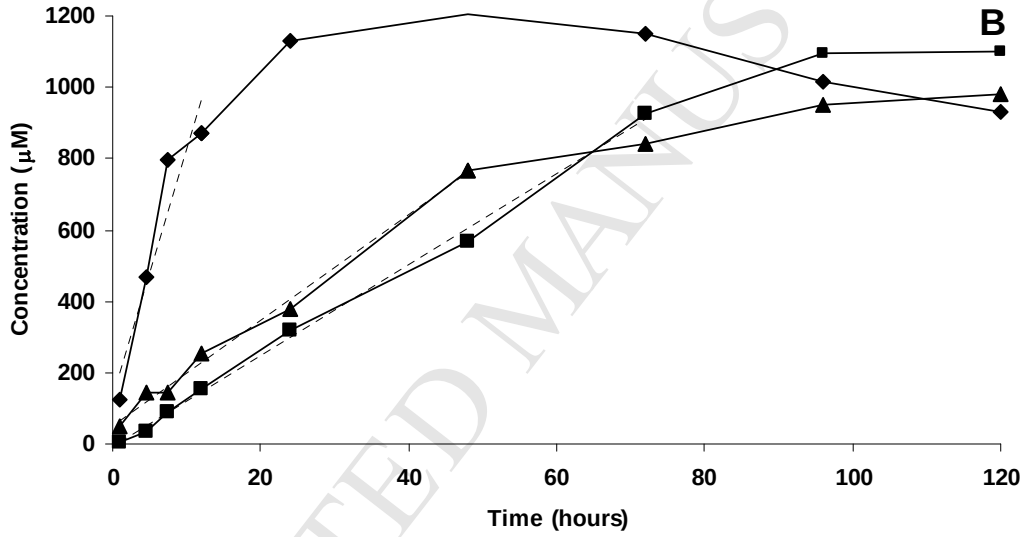

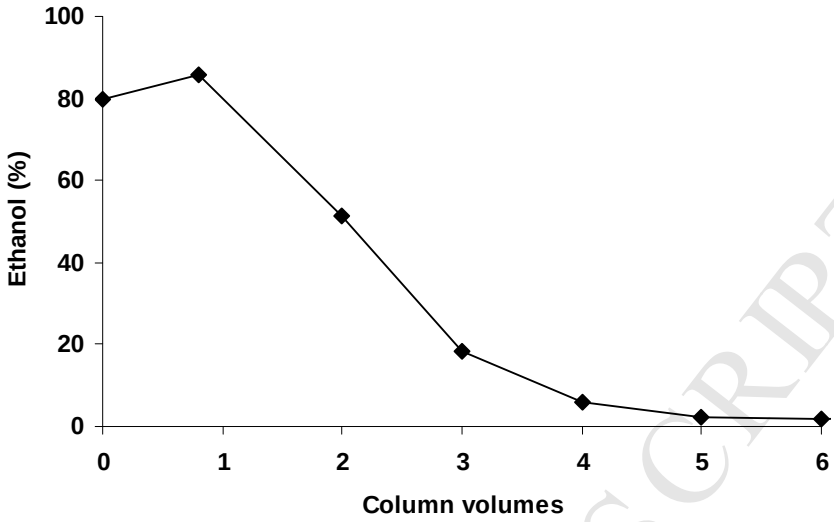

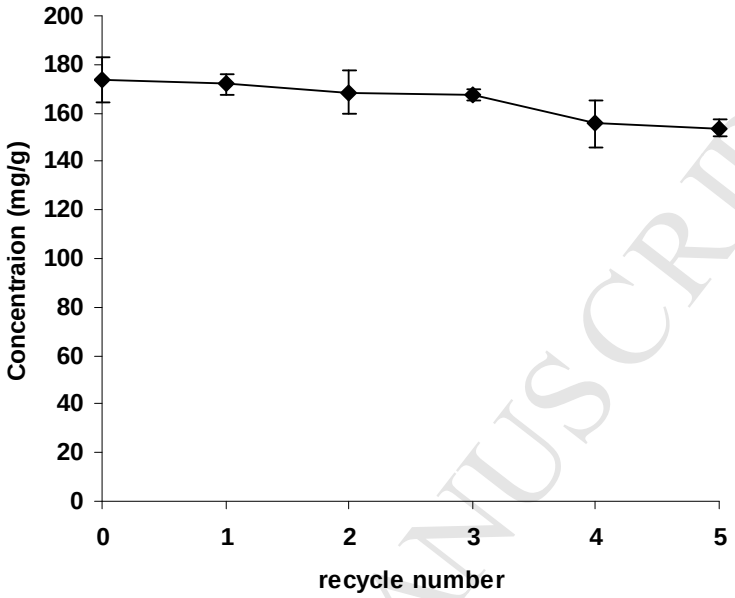

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